XI.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.*

ON THE DIIODBROMACRYLIC AND CHLORBROMACRYLIC ACIDS.

By C. F. Mabery and Rachel Lloyd.

Presented by H. B. Hill.

The readiness with which brompropiolic acid unites with the halogens and the haloid acids to form members of the acrylic acid series has been described by Prof. H. B. Hill,† and certain of these addition products have been studied in detail by him and one of us.‡

The products which result by the action of iodine and of hydrochloric acid on brompropiolic acid will be described in this paper.

Diiodbromacrylic Acid, $C_3I_2BrO_2H$.

Diiodbromacrylic acid is formed when brompropiolic acid is allowed to stand for some time with a solution of iodine in ether. As this method of preparation was found to be somewhat tedious from the length of time required to complete the reaction, we tried the effect of raising the temperature. Brompropiolic acid, with a slight excess over the calculated weight of iodine and five parts by weight of ether, was heated for two hours under a return condenser on the water bath. The residue left after the evaporation of the ether was extracted with successive portions of warm water, and the solution concentrated by evaporation. Diiodbromacrylic acid was deposited from this solution, on cooling, in glistening plates, which were purified by recrystallization from hot water.

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* This research was conducted in connection with the Summer Course of Instruction in Chemistry. C. F. M.

† Berichte der deutsch. chem. Gesellsch., 1879, p 660.

‡ These Proceedings, p. 211.

The yield of pure product by this method has been about sixty per cent of the amount theoretically required. The mother liquors of the first crystallizations gave by evaporation an oily product, which solidified on standing, but which could be purified only with considerable difficulty. This substance crystallizes in flat, white, six-sided plates, very sparingly soluble in cold water, readily in hot, and very soluble in ether, alcohol, carbonic disulphide, and ligroin. It melts at 160°, and sublimes slowly at higher temperatures, apparently unchanged. A yellow coating is formed on the surface when it is exposed to the action of light, yet the decomposition by nitric acid in the estimation of the halogens is not complete below 300°.

The following results were obtained by analysis: —

0.5188 grm. substance gave 0.1682 grm. CO_2 and 0.0180 grm. H_2O.
0.2004 grm. substance gave by Carius' method 0.3276 grm. AgI + AgBr.

	Calculated for $C_3I_2BrO_2H$.	Found.
C	8.93	8.84
H	.25	.39
I_2 + Br	82.87	82.96

The solubility in cold water was determined by the method of V. Meyer. The filtered solution was neutralized with baric carbonate, evaporated to dryness, and the barium estimated by ignition with sulphuric acid.

I. 11.7286 grm. solution gave 0.0707 grm. $BaSO_4$.
II. 13.3239 grm. solution gave 0.0793 grm. $BaSO_4$.

The solution, saturated at 20°, contains, therefore, the percentages: —

I.	II.
2.08	2.05

Hence diiodbromacrylic acid requires for solution 48.37 parts water at 20°.

Salts of Diiodbromacrylic Acid.

Baric Diiodbromacrylate, $Ba(C_3I_2BrO_2)_2.4H_2O$. A solution of the acid was heated with an excess of baric carbonate, filtered, and concentrated by evaporation. The salt crystallized, on cooling, in flat prisms arranged in stellate groups. It is very soluble in hot, less soluble in cold, water.

I. 0.8805 grm. air-dried salt gave 0.0638 grm. H_2O at 80°.
II. 0.8981 grm. air-dried salt gave 0.0629 grm. H_2O at 80°.
III. 0.8049 grm. anhydrous salt gave 0.2002 grm. $BaSO_4$.

	Calculated for $Ba(C_3I_2BrO_2)_2.4H_2O$.	Found. I.	II.
H_2O	7.11	7.24	7.00

	Calculated for $Ba(C_3I_2BrO_2)_2$.	Found.
Ba	14.55	14.62

To determine the solubility in cold water, a hot solution was kept at 20° for four hours, with occasional stirring. The filtered solution was evaporated to dryness, and the barium estimated by ignition with sulphuric acid.

I. 3.2417 grm. solution gave 0.1218 grm. $BaSO_4$.
II. 7.0500 grm. solution gave 0.2665 grm. $BaSO_4$.

This solution contains, therefore, the following percentages: —

I.	II.
15.17	15.26

Taking the mean of these results, this salt requires for solution 6.571 parts water at 20°.

Calcic Diiodbromacrylate, $Ca(C_3I_2BrO_2)_2$. This salt was prepared by neutralizing a solution of the acid with calcic carbonate, and evaporating the filtered solution. The salt crystallizes in branching needles, which are very soluble in water.

0.5995 grm. of the air-dried salt lost 0.0031 grm. at 80°.

This was probably due to the presence of a trace of hygroscopic moisture.

0.5964 grm. of the salt, dried at 80°, gave 0.0945 grm. $CaSO_4$.

	Calculated for $Ca(C_3I_2BrO_2)_2$.	Found.
Ca	4.74	4.66

Argentic Diiodbromacrylate, $AgC_3I_2BrO_2$. Argentic nitrate, added to a solution of the acid, caused a voluminous precipitate of the silver salt, which was washed and dried over sulphuric acid for analysis. It forms oblique prisms, very slightly soluble in cold water, but readily soluble in dilute nitric acid.

0.9585 grm. salt gave 0.2677 grm. AgCl.

	Calculated for $AgC_3I_2BrO_2$.	Found.
Ag	21.17	21.02

Potassic Diiodbromacrylate, $KC_3I_2BrO_2.2H_2O$. A solution of the acid was neutralized with potassic carbonate, and evaporated on the water bath. On cooling, the salt separated in the form of oblique prisms, which are quite soluble in water.

1.8818 grm. of the air-dried salt gave 0.1381 grm. H_2O at 80°.

1.7460 grm. anhydrous salt gave 0.3347 grm. K_2SO_4.

	Calculated for $KC_3I_2BrO_2.2H_2O$.	Found.
H_2O	7.55	7.33

	Calculated for $KC_3I_2BrO_2$.	Found.
K	8.87	8.50

Chlorbromacrylic Acid, $C_3ClBrC_2H_2$.

Chlorbromacrylic acid may be made by the action of ordinary fuming hydrochloric acid on brompropiolic acid. This reaction, however, takes place slowly in the cold; and, although the application of heat causes a more rapid formation of the chlorbromacrylic acid, it produces a secondary decomposition which renders the purification of the product somewhat difficult. We therefore tried the action of hydrochloric acid saturated at 0°. The acid solution soon became filled with crystals of the addition product; and after standing twenty-four hours the reaction was complete. The excess of hydrochloric acid was removed by decantation, and by pressure between folds of filter paper, and the chlorbromacrylic acid was purified by crystallization from hot water. It separates as an oily liquid from a hot aqueous solution; but when nearly cold it crystallizes, forming elongated, flat prisms or needles.

This acid melts at 70°, and sublimes quite freely at a somewhat higher temperature. It is much more soluble in hot than in cold water, and readily soluble in ether, alcohol, benzol, and carbonic disulphide. Its composition was determined by the following analyses: —

0.4462 grm. substance gave 0.3126 grm. CO_2 and 0.0337 grm. H_2O.

0.1792 grm. substance gave, by the method of Carius, 0.3186 grm. AgCl + AgBr.

	Calculated for $C_3ClBrO_2H_2$.	Found.
C	19.40	19.11
H	1.08	.84
Cl + Br	62.26	61.94

The solubility of this acid in cold water was determined by the same method as the diiodbromacrylic acid.

I. 11.6861 grm. solution gave 0.4178 grm. $BaSO_4$.
II. 14.4534 grm. solution gave 0.5264 grm. $BaSO_4$.

The solution, saturated at 20°, contains the percentages: —

I.	II.
5.69	5.80

The mean of these results gives 17.41 parts as the quantity of water required for solution at 20°.

Salts of Chlorbromacrylic Acid.

The salts of this acid were made by the same methods as the corresponding salts of diiodbromacrylic acid.

Baric Chlorbromacrylate, $Ba(C_3ClBrO_2H)_2.2H_2O$. This salt crystallizes in flattened prisms, which belong apparently to the monoclinic system. Its composition was established by the following analyses: —

I. 0.3730 grm. air-dried salt gave 0.0263 grm. H_2O at 80°.
II. 0.6283 grm. air-dried salt gave 0.0437 grm. H_2O at 80°.
III. 0.3467 grm. anhydrous salt gave 0.1606 grm. $BaSO_4$.
IV. 0.4468 grm. anhydrous salt gave 0.2053 grm. $BaSO_4$.

	Calculated for $Ba(C_3ClBrO_2H)_2.2H_2O$.	Found. I.	II.
H_2O	6.64	7.05	6.96

	Calculated for $Ba(C_3ClBrO_2H)_2$.	Found. III	IV.
Ba	27.07	27.23	27.02

The solubility in cold water was determined by the method of V. Meyer.

I. 2.8936 grm. solution gave 0.1914 grm. $BaSO_4$.
II. 5.1385 grm. solution gave 0.3378 grm. $BaSO_4$.

From these results the following percentages were calculated: —

I.	II.
14.06	14.28

This salt, therefore, requires for solution 6.985 parts of water at 20°.

Calcic Chlorbromacrylate, $Ca(C_3ClBrO_2H)_2.4H_2O$. This salt forms branching needles, which are very soluble in hot, less soluble in cold, water.

I. 0.4981 grm. air-dried salt gave 0.0762 grm. H_2O at 80°.
II. 0.6211 grm. air-dried salt gave 0.0956 grm. H_2O at 80°.
III. 0.4219 grm. anhydrous salt gave 0.1424 grm. $CaSO_4$.
IV. 0.5096 grm. anhydrous salt gave 0.1713 grm. $CaSO_4$.

	Calculated for $Ca(C_3ClBrO_2H)_2.4H_2O$.	Found. I.	II.
H_2O	14.97	15.30	15.39

	Calculated for $Ca(C_3ClBrO_2H)_2$	Found. III.	IV.
Ca	9.78	9.93	9.87

Argentic Chlorbromacrylate, $Ag(C_3ClBrO_2H)_2$. This salt was precipitated by the addition of argentic nitrate and ammonic hydrate to a solution of the acid. It forms microscopic needles, which are almost insoluble in cold water.

I. 0.2760 grm. salt gave 0.1337 grm. AgCl.
II. 0.3445 grm. salt gave 0.1668 grm. AgCl.

	Calculated for $Ag(C_3ClBrO_2H)$.	Found. I.	II.
Ag	36.93	36.47	36.88

Potassic Chlorbromacrylate, KC_3ClBrO_2H. This salt forms clusters of irregular, pointed, anhydrous prisms, which are less soluble in cold than in hot water.

0.5346 grm. salt, dried at 80°, gave 0.2132 grm. K_2SO_4.

	Calculated for KC_3ClBrO_2H.	Found.
K	17.49	17.91

The addition of bromine to chlorbromacrylic acid takes place very readily at the ordinary temperature, with the formation of chlortribrompropionic acid. A solution of the acid in chloroform was allowed to stand several days, with somewhat more than the calculated weight of bromine. Chlortribrompropionic acid separated from this solution in large prismatic crystals, which after crystallization from carbonic disulphide melted at about 98°. This acid will be submitted to a more extended study.